Oxidation Stability of Biodiesel and Biodiesel Blends

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Steve Goguen and Dennis Smith, Managers

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Objectives

• Determine if B100 stability can be predicted by accelerated tests
• Determine if B100 stability is predictive of the stability of B5 and/or B20 blends
• Relate accelerated stability test results to more real world scenarios
• Recommend stability test methods and limits for B100, B20, and B5 blends
Stability Study Approach

- Perform accelerated stability tests on 19 B100 samples covering the range available in US
- Select 8 B100 covering the range of stability for:
  - 12 week storage tests
  - Blending with 6 diesel fuels to produce 48 B5 and 48 B20 blends
  - Perform accelerated stability tests on the B5 and B20 blends
- Select 8 B5 and 8 B20 blends for:
  - 12 week storage test
  - One week test simulating fuel tank ageing
  - High temperature test simulating conditions in an engine fuel injection system
- Interpret results to address study objectives
Accelerated Stability Tests

• Lab tests that reveal if a sample is stable or unstable in a short time
  – Oxidize under severe or “accelerated” conditions

• Two main approaches:
  – Induction period - How long till oxidation starts?
  – Deposit formation – How much gum or deposit forms after oxidation for a fixed time?
B100 Stability

**Induction Time**
- Rancimat test, EN14112 (110°C/air)
- Measures induction time for volatile acid formation (hr)
  - May be related to resistance to oxidation or oxidation reserve, or time for start of deposit formation
- Included in European biodiesel quality specification

**Deposit Formation**
- ASTM D2274M (95°C/Oxygen/16 hr)
- Filter sample to measure insoluble formation
- Wash vessel and filter to measure gum formation
- Total insoluble=filterable+gum (mg/100 ml)
- Commonly used to specify diesel stability for pipeline transport
Thermal Stability

- Reflectance all over 90%
- B100 is thermally stable on this test
- Independent of oxidation stability
Distinguishing Stable and Unstable Samples

- i-Octane insoluble may be more predictive of what happens in diesel blends
- Bimodal distribution, 14 stable samples, 5 unstable

- There will be no big increase in i-octane insoluble if EN14112 (Rancimat) is above about 3 to 4
Correlation Between Methods for B100

- **EN14112 IP and D2274 Total Insoluble**
  - Approximate correlation
  - Rancimat of 3 – 4 hr ensures insoluble below 2.5 mg/100 ml (with one exception)

- **Total Insoluble and i-Octane Insoluble**
  - Samples with high total insoluble have high i-octane insoluble
  - If total insoluble is below roughly 2.5 mg, i-octane insoluble is low (limit may actually be as high as 7 to 8)
Rancimat vs OSI

Rancimat (EN14112) and OSI are similar instruments made by two different manufacturers
- operate on identical principle
- Bubbling air through sample, capturing volatile oxidation products in water, measuring change in water conductivity

Results are similar but not identical

With some OSI method refinement it seems likely that identical results could be obtained

Rancimat from Bosch, OSI from Eastman
Antioxidant Effectiveness

- Simple demonstration that AO can be effective for both induction time and deposits
- Ongoing work to determine impact on blends
**B100 Downselection**

- Cover range on all tests
- Cover all feedstocks
- Samples to be used in:
  - 12-week storage test
  - Preparation of B5 and B20 blends

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Rancimat</th>
<th>D525</th>
<th>D2274 Total</th>
<th>D2274 i-Octane</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL-27128-F Canola</td>
<td>4.2 (med)</td>
<td>341 (med)</td>
<td>6.5 (med)</td>
<td>198 (high)</td>
</tr>
<tr>
<td>AL-27129-F Palm Stearin</td>
<td>3.1 (med)</td>
<td>169 (med)</td>
<td>1.9 (low)</td>
<td>2.6 (low)</td>
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<tr>
<td>AL-27137-F Soy</td>
<td>6.5 (high)</td>
<td>retesting</td>
<td>1.0 (low)</td>
<td>2.6 (low)</td>
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<td>AL-27138-F Soy</td>
<td>0.5 (low)</td>
<td>80 (low)</td>
<td>7.6 (med)</td>
<td>4.4 (low)</td>
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<tr>
<td>AL-27141-F Soy</td>
<td>5.5 (high)</td>
<td>335 (med)</td>
<td>0.3 (low)</td>
<td>0.6 (low)</td>
</tr>
<tr>
<td>AL-27148-F Grease</td>
<td>7.8 (high)</td>
<td>325 (med)</td>
<td>0.9 (low)</td>
<td>19 (med)</td>
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<tr>
<td>AL-27152-F Rapeseed</td>
<td>7.3 (high)</td>
<td>418 (med)</td>
<td>0.5 (low)</td>
<td>6.4 (low)</td>
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<tr>
<td>AL-27160-F Tallow</td>
<td>0.2 (low)</td>
<td>159 (low)</td>
<td>17.6 (high)</td>
<td>124 (high)</td>
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</table>
### Additional B100 Properties

<table>
<thead>
<tr>
<th></th>
<th>AL-27128</th>
<th>AL-27129</th>
<th>AL-27137</th>
<th>AL-27138</th>
<th>AL-27141</th>
<th>AL-27148</th>
<th>AL-27152</th>
<th>AL-27160</th>
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<tbody>
<tr>
<td><strong>Particulate Contamination</strong></td>
<td>D 6217, mg/l</td>
<td>14.7</td>
<td>0.2</td>
<td>103.9</td>
<td>3.5</td>
<td>19.5</td>
<td>5.1</td>
<td>17.6</td>
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<tr>
<td><strong>Total Water</strong></td>
<td>D 6304, ppm</td>
<td>656</td>
<td>217</td>
<td>149</td>
<td>131</td>
<td>118</td>
<td>298</td>
<td>1092</td>
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<td><strong>Flash Point</strong></td>
<td>D 93, °C</td>
<td>160</td>
<td>177</td>
<td>179</td>
<td>152</td>
<td>169</td>
<td>178</td>
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<td><strong>Acid Number</strong></td>
<td>D664, mg KOH/g</td>
<td>0.23</td>
<td>0.41</td>
<td>0.05</td>
<td>0.33</td>
<td>0.13</td>
<td>0.69</td>
<td>0.09</td>
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<tr>
<td><strong>Free Glycerin</strong></td>
<td>D6458, wt%</td>
<td>0.009</td>
<td>&lt;0.001</td>
<td>0.002</td>
<td>0.002</td>
<td>0.005</td>
<td>&lt;0.001</td>
<td>0.001</td>
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<tr>
<td><strong>Total Glycerin</strong></td>
<td>D6458, wt%</td>
<td>0.103</td>
<td>0.081</td>
<td>0.144</td>
<td>0.016</td>
<td>0.121</td>
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<td><strong>Elemental Analysis</strong></td>
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<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td></td>
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<tr>
<td>IsoOctane Insoluble</td>
<td>D 4625, mg/100 ml</td>
<td>3.9</td>
<td>0.1</td>
<td>1.9</td>
<td>2.3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Peroxide Value</td>
<td>D 3703, mg</td>
<td>217.28</td>
<td>105.33</td>
<td>12.8</td>
<td>98.21</td>
<td>8.78</td>
<td>43.84</td>
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<td>Viscosity@40°C</td>
<td>D 445,</td>
<td>4.45</td>
<td>5.12</td>
<td>4.10</td>
<td>4.09</td>
<td>4.67</td>
<td>4.47</td>
<td>4.86</td>
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<td>Polymer Content</td>
<td>ISO 16931</td>
<td>2.63</td>
<td>0.17</td>
<td>0.82</td>
<td>1.03</td>
<td>1.46</td>
<td>2.17</td>
<td>4.91</td>
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</table>
# Diesel Fuel Properties

• 5 ULSD, 1 LSD

• Fuels that were available in Dec. 2005 – may not be fully representative of what ULSD will actually look like

• 3 ULSD look more like No. 1 fuels than No. 2

<table>
<thead>
<tr>
<th>Sample:</th>
<th>ASTM D975 Limit (No. 2 Diesel)</th>
<th>AL27150F</th>
<th>AL27151F</th>
<th>AL27166F</th>
<th>AL27171F</th>
<th>AL27175F</th>
<th>AL27176F</th>
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</thead>
<tbody>
<tr>
<td>Flash Point, °C</td>
<td>52</td>
<td>56</td>
<td>69</td>
<td>59</td>
<td>73</td>
<td>59</td>
<td>69</td>
</tr>
<tr>
<td>Sulfur, ppm</td>
<td>15 or 500</td>
<td>7.4</td>
<td>6.7</td>
<td>5.8</td>
<td>339.6</td>
<td>2.9</td>
<td>7.4</td>
</tr>
<tr>
<td>T90, °C</td>
<td>282 min</td>
<td>274</td>
<td>313</td>
<td>269</td>
<td>319</td>
<td>333</td>
<td>236</td>
</tr>
<tr>
<td>Carbon Residue (10%), mass%</td>
<td>0.35</td>
<td>0.07</td>
<td>0.04</td>
<td>0.06</td>
<td>0.13</td>
<td>0.05</td>
<td>0.08</td>
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<tr>
<td>Acid Number, mg KOH/g</td>
<td>none</td>
<td>0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Peroxide Number</td>
<td>none</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Water and Sediment, vol%</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
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<tr>
<td>Ash Content, mass%</td>
<td>0.01</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Total Aromatics, mass%</td>
<td>none</td>
<td>15.7</td>
<td>22.1</td>
<td>18.1</td>
<td>36.2</td>
<td>8.2</td>
<td>19.3</td>
</tr>
<tr>
<td>Monoaromatics, mass%</td>
<td>none</td>
<td>14.4</td>
<td>19.9</td>
<td>17.1</td>
<td>27.6</td>
<td>7</td>
<td>17.4</td>
</tr>
<tr>
<td>Polynuclear Aromatics, mass%</td>
<td>none</td>
<td>1.3</td>
<td>2.1</td>
<td>1</td>
<td>8.7</td>
<td>1.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Total Insolubles, mg/100 ml</td>
<td>none</td>
<td>0.25</td>
<td>0.25</td>
<td>0.5</td>
<td>0.2</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Thermal Stability, 150°C/180 min % Reflectance</td>
<td>none</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>--</td>
<td>95</td>
<td>100</td>
</tr>
<tr>
<td>Particulate Contamination, mg/L</td>
<td>none</td>
<td>0.5</td>
<td>0.4</td>
<td>0.8</td>
<td>0.8</td>
<td>1.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Most B5 samples highly stable for induction time or deposits
Can B100 Stability Ensure B5 Stability?

Yes, B100 stability appears to be an excellent predictor of blend stability, a Rancimat of 3 hr ensures low deposits and long induction time for the blend.
Additional B5 Stability Data

B100 samples producing less than 2.5 mg/100 ml on D2274M produce stable (<2.5 mg/100 ml) B5 blends
B5 blends are thermally stable if produced from oxidatively stable B100
Preliminary B20 Results

- Most samples are stable, but a range of stability is observed
- Consistent IP and deposit results
Can B100 Stability Ensure B20 Stability?

Yes, B100 stability appears to be an excellent predictor of blend stability, 3 hour Rancimat ensures low deposits and 6 hr Rancimat in the blend (with one exception out of 48 samples)
B100 samples producing less than 2.5 mg/100 ml on D2274M produce stable (<2.5 mg/100 ml) B20 blends.
B20 blends are thermally stable if produced from oxidatively stable B100.
Tentative Conclusions

• Blend stability is dominated by B100 stability
• A 3 hr Rancimat IP for B100 appears to be adequate to ensure stability of both B5 and B20 blends
  – IP may need to be longer than 3 hr at point of production to insure stability at point of blending
• It is likely that OSI can be an alternative method to Rancimat
• Currently also investigating D525 as alternative
What is missing?

• Only accelerated stability test data reported to date

• Need results of more realistic tests
Ageing Scenarios

1. In storage and handling
   - Applies to B100 and blends

2. In vehicle fuel tank
   - Recirculation at low fuel level
   - Applies to biodiesel blends only

3. Ageing in high temperature engine fuel system
   - Deposit formation from unstable or pre-aged fuel
   - Applied to biodiesel blends only
Tests to Simulate Ageing Scenarios

1. *Ageing in storage: D4625*
   - Quiescent ageing at 43°C for 12 weeks
   - Measurement of total insoluble plus other fuel properties

2. *Vehicle tank ageing: D4625 (heavily modified)*
   - Quiescent ageing at 80°C for 1 week
   - With ullage purge to insure test is not oxygen limited
   - Measurement of total insoluble plus other fuel properties

3. *High temperature fuel system ageing*
   - Quiescent ageing at 80°C for 1 week (as above)
   - Followed by ASTM D6468 at 150°C/180 min/350 ml sample size
   - Gravimetric measurement of insoluble plus other fuel properties
Summary and Future Work

• Preliminary data suggests that ensuring B100 stability might also ensure the stability of B5 and B20 blends

• Realistic simulation tests are ongoing, anticipate full report published by October 2006

B100 results are available here: http://www.nrel.gov/vehiclesandfuels/npbf/pdfs/39721.pdf

This presentation will also be posted on NREL’s website within a few weeks